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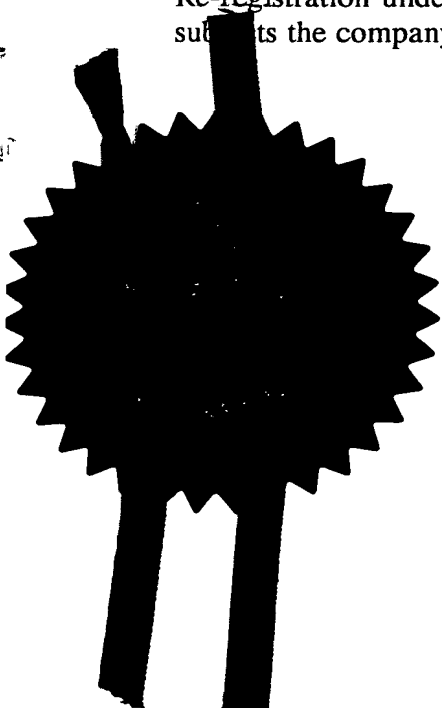
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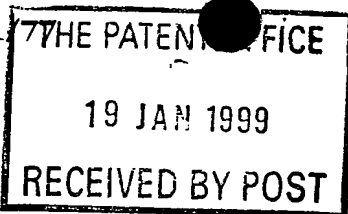
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2. Patent application number (The Patent Office will fill in this part)	19 JAN 1999		<b>9901031.6</b>
3. Full name, address and postcode of the or of each applicant (underline all surnames)	Reflective Technology Industries Ltd Road One Winsford Industrial Estate Winsford Cheshire CW7 3QQ		
Patents ADP number (if you know it)			
If the applicant is a corporate body, give the country/state of its incorporation	GB 6449227003 /		
4. Title of the invention	Retroreflective Inks		
5. Name of your agent (if you have one)	McNeight & Lawrence		
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	Regent House Heaton Lane Stockport Cheshire SK4 1BS		
Patents ADP number (if you know it)	0001115001 /		
6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of filing (day / month / year)
7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing (day / month / year)	
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Description 18

Claim(s) 7

Abstract

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## **RETROREFLECTIVE INKS**

This invention relates to retroreflective inks and methods for making them.

Retroreflective coating compositions have been the subject of numerous patents, for example US Patents 2 963 378, Palmquist *et al*, 3 099 637, 3 228 897 and 3 420 597, Nellessen, 3 535 019, Longlet *et al* and 4 103 060 and 4 263 345, Bingham *et al*. A retroreflective ink has been commercially available for a number of years, marked by the 3M company, this product being available in dark grey and sold as a three pack system, comprising a binder dispersion system, a pack of hemispherically coated glass microspheres or beads and a coupling agent, which are mixed just prior to use.

One pack inks were proposed in WO 94/06869, M N Ellis and in EP 0 729 592, Reflective Technology Industries Limited and US 5 650 213, Reflective Technology Inc., which also disclose the incorporation of pigment. US 5 650 213 specified a range of pigment particle size which is what is, in fact, the usual range commercially available, and ranges of binder/bead and binder/(bead and pigment) volume ratios which are seemingly the ranges of choice to produce an ink which is printable by conventional screen printing techniques.

Problems associated with the performance of reflective coatings, especially in the convenient, one-pack form that does not require mixing just prior to printing, involve shelf life, washfastness and abrasion resistance. These key areas are interrelated - the binder system must be such as will not allow the beads to settle even over extended storage periods, and it must also not couple to the beads during that storage, yet it must, on printing, adhere the beads to the substrate in a reasonably washfast and abrasion resistant manner while permitting the beads to be exposed appropriately to retroreflect light.

The severity of these problems may explain the sale by 3M of the three pack system and the fact that the inks produced according to US 5 650 213 are formulated solely for the production of printed fabric by the patentee Reflective Technology Inc. and not for sale to printers.

The present invention addresses these - and other - problems and provides long shelf life one pack retroreflective ink systems with good washfastness and abrasion resistance.

The invention, in one aspect, comprises a one-pack retroreflective ink comprising microbeads in a liquid carrier medium including binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied, and a coupling agent which couples the microbeads and cross-links the binder chemicals, characterised in that the coupling agent is unreactive except at elevated temperature at which the ink on the substrate is cured.

The invention, in another aspect, comprises a one-pack or a two-pack retroreflective ink comprising microbeads in a liquid carrier medium including binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied, the microbeads being incorporated in the carrier medium, and a coupling agent which couples the microbeads and cross-links the binder chemicals, characterised in that the coupling agent is not activated until the ink is printed.

The two-pack system comprises a separate pack for the coupling agent.

The ink may comprise retroreflective and/or non-retroreflective microbeads.

The binder system may comprise polyvinylidene chloride copolymer and the coupling agent comprise (3-aminopropyl) silanetriol.

The binder system may comprise polyvinylidene chloride copolymer and the coupling agent comprise blocked 1, 6 hexamethylene diisocyanate trimer.

The binder system may comprise polyurethane and the coupling agent comprise blocked 1, 6 hexamethylene diisocyanate trimer.

The microbeads may have an aluminium coating, and may be pre-treated with a silicate before inclusion in the ink. They may be pretreated with sodium silicate. They may be treated with an amino silane, which treatment may be after a silicate treatment and before inclusion in the ink. The amino silane may be bis-[*gamma*-(trimethoxysilyl) propyl] amine.

The ink may comprise pigment, and may, especially when comprising pigment, comprise non-retroreflective, which usually means un-metallised, beads.

The microbeads may be pretreated before metallisation with stannous chloride.

The ink may be formulated - as to, e.g. their viscosity, particle size - suitably for screen printing. The microbeads may be 40 micron beads, and are, for best retro-reflectivity, of high, e.g. 1.9, refractive index glass.

The ink may comprise a humectant, which may comprise urea and/or 2,3 propanediol, and may be water-based. It may comprise a buffer, to ensure an appropriate pH, such buffer, for example, comprising an ammonium phosphate buffer or a sodium

phosphate buffer. A dispersant may also be included, as may a defoamer, a thickening agent, a cross-linking agent and a softening agent.

Non-water based inks may also be comprised within the invention. In this case, the need to protect the aluminium coating against attack in water-based media may be less important.

Surprisingly, having regard to the teaching of US 5 650 213, substantially better quality inks - in terms of reflectivity, washfastness, abrasion resistance and shelf life - are produced with binder to bead volume ratios equal to or less than 50%. Essentially, more beads can be attached using less obscuring binder, more firmly and more permanently than when the prior art binder to bead ratios are used.

For a screen printing ink, the viscosity is desirably equal to or less than 40 pascals at room temperature.

The invention also comprises a method for making a one-pack retroreflective ink comprising the steps of:

- making microbeads;
- suspending the microbeads in a liquid carrier medium;
- the liquid carrier medium comprising binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied and a coupling agent which couples the microbeads and cross-links the binder chemicals, the coupling agent being unreactive except at elevated temperature at which the printed substrate is cured.



The method comprises applying an aluminium coating to glass microbeads. The microbeads may be pretreated with stannous chloride prior to application of the aluminium coating, and may be treated with a dilute solution of stannous chloride.

The microbeads may be hemispherically metallised in a vacuum metallising process in which they are held on a film with an adhesive coating for transport through the metallising process, the adhesive coating comprising a styrene/butadiene type or other adhesive, which loses its tack when wet. The film may comprise a polyester film. Following metallisation, the film may be passed through an aqueous solution of citric acid or other aqueous solution with a  $pK_a$  value of around 2, and may be treated ultrasonically to assist in release of the microbeads from the adhesive surface. In contradistinction to other method for attachment of beads for metallisation, this method is easier at least inasmuch as the citric acid bath can be re-used over and over without replenishment.

The microbeads may be treated prior to inclusion in the ink with a silicate, which may be a dilute aqueous solution of sodium silicate. The beads may also (with or without such sodium silicate treatment) be treated with an amino silane prior to inclusion in the ink, and such amino silane treatment may follow the silicate treatment. A particularly beneficial amino silane is bis- $[\gamma$ -(trimethoxysilyl) propyl] amine. These treatments, severally and collectively, appear to enhance the permanence of the attachment of the aluminium coating to the microbeads and of the microbeads to the substrate on printing.

An amino silane - which could be the same amino silane used to treat the microbeads - may also be added to the liquid carrier medium as coupling agent, in the event, see below, that a two-pack, rather than a one-pack system is required.

In the preparation of the ink, a liquid carrier medium may be prepared comprising binder chemicals and coupling agent, the microbeads being added to the medium. A pigment may be added to the medium containing the microbeads.

A humectant may be incorporated in the medium, as may a buffer, a dispersant, a defoamer and a thickener. The thickener may be added to the medium in two steps, namely before and after the addition of the binder and coupler.

A softener may also be added to the medium.

Inks and methods for making them, according to the invention, will now be described with reference to the accompanying drawings, in which:-

Figure 1 is a diagrammatic illustration of the production of metallised beads; and

Figure 2 is a block diagram of a process for making an ink.

Ink formulations according to the invention are shown in Tables 1 to 4.

**Table 1** - inks based on a acrylic copolymer binder system and (3-aminopropyl) silanetriol coupling agent

<b>Ingredient/Ink reference</b>	<b>C202</b>	<b>C205</b>	<b>C208</b>
Urea (Humectant)	10	10	10
Water	154	179	179
Ammonium phosphate buffer	20	20	20
Alcoprint PDN (Dispersant)	2	2	2
Agitan 218 (Defoamer)	2	2	2
Alcoprint PT21 (Thickening agent)	8	8	8
2,3 Propane diol (Humectant)	25	25	25
Alcoprint PFL (Trimethoxymethyl melamine cross-linking agent)	15	15	15
Alcoprint PSM (Softening agent)	30	30	30
Alcoprint PBA (Acrylic copolymer binder)	300	225	225
Ammonium hydroxide	1	1	1
Silquest VS-142 (3-aminopropyl silanetriol coupling agent)			
[20% in water]	25	25	25
Alcoprint PT21 (Thickening agent)	6	3	4.6
Metallised beads (40 micron) treated with sodium silicate and Silquest A-1170 (Bis[trimethoxysilylpropyl] amine)	400	450	400
Nonmetallised beads (40 micron) treated with sodium silicate and Silquest A-1170	--	--	50
<b>Total</b>	<b>997</b>	<b>995</b>	<b>996.6</b>
Binder volume %	12	9	9
Bead volume %	16	18	18
Binder volume/bead volume %	75	50	50
Viscosity	20.7	16.2	23.2
Temperature	16.6	16.6	16.6
pH	8.4	8.9	8.8

**Table 2 -** inks based on a polyvinylidene chloride copolymer binder system and (3-aminopropyl) silanetriol coupling agent

<b>Ingredient/Ink reference</b>	<b>V246</b>	<b>V248</b>	<b>V251</b>
Urea (Humectant)	10	10	10
Water	128	288	288
Ammonium phosphate buffer	20	20	20
Emulsifier WN (Dispersant)	3	3	3
Agitan 218 (Defoamer)	2	2	2
Alcoprint PT21 (Thickening agent)	8	8	8
2,3 Propane diol (Humectant)	25	25	25
Polidene 33-048 (Binder)	273	163	163
Ammonium hydroxide	1.4	1.4	1.4
Silquest VS-142 (Coupling agent) [20% in water]	25	25	25
Alcoprint PT21 (Thickening agent)	3	5	3
Metallised beads (40 micron) treated with sodium silicate and Silquest A-1170	500	450	400
Non-metallised beads (40 micron) treated with sodium silicate and Silquest A-1170	--	--	50
<b>Total Weight of Ink (g)</b>	<b>998.4</b>	<b>1,000.4</b>	<b>998.4</b>
 Binder volume %	 15	 9	 9
Bead volume %	20	18	18
Binder volume/bead volume %	75	50	50
 Viscosity (pascals)	 25.6	 14.2	 12.3
Temperature (°C)	17.7	17.6	17.2
pH	8.6	8.7	8.7

**Table 3 -** inks based on a polyvinylidene copolymer binder system and a combination of (3-aminopropyl) silanetriol and blocked hexamethylene diisocyanate trimer coupling agents

<b>Ingredient/Ink reference</b>	<b>V253</b>	<b>V254</b>	<b>V257</b>
Urea (Humectant)	10	10	10
Water	91	183	183
Ammonium phosphate buffer	20	20	20
Emulsifier WN (Dispersant)	2	2	2
Emulsifier HVN (Dispersant)	2	2	2
Agitan 218 (Defoamer)	2	2	2
Alcoprint PT21 (Thickening agent)	9.3	8	8
2,3 Propane diol (Humectant)	25	25	25
Polidene 33-048 (Binder)	273	181	181
Ammonium hydroxide	1.4	1.4	1.4
Silquest VS-142 (Coupling agent) [20% in water]	25	25	25
Trixene BI 7986 (Coupling agent)	40	40	40
Alcoprint PT21 (Thickening agent)	--	--	--
Metallised beads (40 micron) treated with sodium silicate and Silquest A-1170	500	500	400
Non-metallised beads treated with sodium silicate and Silquest A-1170	--	--	100
<b>Total Weight of Ink (g)</b>	<b>1,000.7</b>	<b>999.4</b>	<b>999.4</b>
Binder Volume %	15	10	10
Bead Columes %	20	20	20
Binder Volume/Bead Volume Ratio %	75	50	50
Viscosity (pascals)	22.5	22.1	21.2
Temperature (°C)	19.3	19.0	19.0
pH	8.4	8.3	8.4

**Table 4 -** inks based on a polyurethane binder system and a blocked 1,6 Hexamethylene diisocyanate trimer coupling agent

<b>Ingredient/Ink reference</b>	<b>P96</b>	<b>P98</b>	<b>P102</b>
Urea (Humectant)	10	10	10
Water	62	187	187
Sodium Phosphate Buffer	10	10	10
Emulsifier WN (Dispersant)	3	3	3
Agitan 218 (Defoamer)	2	2	2
Alcoprint PT21 (Thickener)	3.0	3.1	3.0
2,3 Propane diol (Humectant)	25	25	25.1
Alcoprint PSM (Softener)	30	30	30
Witcobond 769 (Binder)	300	225	226
Trixene BI-7986 (Coupler)	50	50	50
Alcoprint PT21 (Thickener)	0.7	4.0	3.0
Metallised beads treated with sod.silicate and Silquest A-1170	500	450	400
Non-metallised beads treated with sod.silicate and Silquest A-1170	--	--	70
<b>Total Weight of Ink (g)</b>	<b>993.7</b>	<b>999.1</b>	<b>1,019.1</b>
Binder Volume %	12	9	8.8
Bead Volume %	60	18	18.5
Binder Volume/Bead Volume Ratio %	60	50	47.9
Viscosity (pascals)	O/R	31.0	32.0
Temperature (°C)	18.8	18.2	18.5

Generally speaking, the ingredients are added in the tabulated order. The thickener is added in two stages. Pigment, not tabulated, is added at the end in suitable quantity to yield the desired colour.

Viscosities were measured with a Brookfield viscometer using a number 5 spindle rotating at 10 rpm.

Table 5 lists the chemical nature and sources of proprietary products used in the inks of Tables 1 to 4.

**Table 5**

<b>Ink Component</b>	<b>Proprietary Product</b>	<b>Chemical Nature</b>	<b>Supplier</b>
Binder	Alcoprint PBA	Aqueous emulsion of an acrylic copolymer	Allied Colloids
	Polidene 33-048	Aqueous emulsion of a vinylidene chloride/ acrylate copolymer	Scott Bader
	Witcobond 769	Water based polyurethane dispersion	Baxenden
Cross-linking/ coupling agent	Alcoprint PFL	Trimethoxymethyl melamine	Allied Colloids
	Silquest VS-142	3-Aminopropyl silanetriol	OSi Specialities/ Ambersil Ltd.
	Silquest A-1170	bis-trimethoxysilylpropyl) amine	OSi Specialities/ Ambersil Ltd.
	Trixene BI-7986	Blocked 1,6 hexamethylene diisocyanate trimer	Baxenden
Softening agent	Alcoprint PSM		Allied Colloids
Thickening agent	Alcoprint PT21	Dispersion of an acrylic copolymer in light mineral oil	Allied Colloids
Dispersant	Alcoprint PDN	Aqueous solution of an anionic acrylic polymer	Allied Colloids
	Emulsifier WN	Nonionic arylpolyglycol ether	Bayer

<b>Ink Component</b>	<b>Proprietary Product</b>	<b>Chemical Nature</b>	<b>Supplier</b>
	Emulsifier HVN		BASF
Defoaming agent	Agitan 218		Munzing Chemie

Retroreflective microbeads are made, according to one aspect of the invention, by a process which is generally similar to the one that has been used commercially for many years, namely by embedding glass microspheres in an adhesive layer on a substrate and coating the exposed surface of the microspheres with an aluminium layer in a vacuum metalliser. There are, however, subtle, but important differences. The method according to the invention, which is novel and inventive *per se* for the manufacture of hemispherically coated microbeads, regardless of any ink formulation in which they will be used is illustrated by way of example in Figure 1.

A carrier material 11, which is for example a polyester film, supplied on a reel 11a, which may contain, say, 1000m of film of width 1500mm, is coated by contact with a lick roller 12 dipping into a bath 13 with an 18 micron layer 14 of a styrene/butadiene type adhesive 15, the coating thickness being determined e.g. by a doctor blade/roller arrangement 16.

Beads 17 (see inset to Figure 1) are scattered on the adhesive layer 14 from a hopper 18 and pressed into the adhesive layer 14 by a roller arrangement 19. Excess beads are removed e.g. by suction arrangement 20.

Glass beads of refractive index 1.9, size 40 microns are used, and, after the roller arrangement 19, appear, in cross-section, as shown in the inset.



The beaded carrier material 11 is then passed through a vacuum metalliser 21 to be coated with aluminium to a thickness of about 0.3 microns. The material 11, wound on a reel, is placed in the vacuum metalliser and run off on to a take-up reel to which it is secured; then the metalliser is evacuated and the aluminium source energised and the material passed reel-to-reel to expose it to the aluminium vapour. The coated, beaded carrier 11 is then passed through a bath 22 of aqueous solution (1%) of citric acid at a temperature of 40 - 50°C, passing over a series of rollers 23 to provide a dwell time in the bath of several minutes. The material 11 also passes over an ultrasonic plate 24 which aids release of the microbeads which fall to the bottom of the bath 22. At the end of the run of 1000m of carrier 11, the microbeads are sucked out of the bottom of the bath 22, rinsed with water and dried.

The effect of the citric acid bath is to cause the styrene/butadiene adhesive to lose its tack and release the microbeads. The material 11 regains its tack on drying, and can be re-used for further runs of bead manufacture without the need for further coating. The citric acid bath 22 can likewise be reused without replenishment of the citric acid.

Prior to coating, the glass beads are pre-treated with a dilute aqueous solution of stannous chloride, followed by drying and resieving. It is found that this gives significant improvement in the durability of the reflectivity of a printed design.

After coating, the beads are treated with a dilute aqueous solution of sodium silicate. It is thought that the treatment passivates the aluminium coating, reducing its susceptibility to attack in aqueous environments, while, at the same time, the sodium silicate reacts with the titanium/barium glass and/or the aluminium increasing the number of reactive sites on the surface of the coated microbeads that are available for reaction with the coupling agent in the ink.

If this sodium silicate treatment is carried out close to the metallisation process, the beads from that process can be used after rinsing but before drying. About 40 kg wet metallised beads (containing some 10 kg water) are mixed with a solution of 20 kg water containing 1.4 kg sodium silicate and stirred for 5 minutes. The beads are then allowed to settle, the sodium silicate solution decanted off, the beads rinsed with tap water, with a final rinse in deionised water.

Significant improvement in washfastness, especially with low (e.g. below 0.5%) levels of certain coupling agents in the formulation (which considerably improves shelf life), is obtained by further treatment of the metallised beads with amino silanes, significantly bis-*[gamma*-(trimethoxysilyl) propyl] amine.

The combined effect of these bead preparation treatments is to provide an ink with a shelf life well in excess of 12 months yet which exhibits insignificant loss of retroreflectivity after multiple washings at 40°C, even if the amount of coupling agent is as low as 0.5%.

Figure 2 is a block diagram of production steps for a typical ink according to the invention, the steps being :

- 30 Glass microbead production, with any necessary sieving to a desired size range - about 40 microns is an ideal size
- 31 Stannous chloride pre-treatment, drying
- 32 Metallising
- 33 Recovery in citric acid solution

- 34 Rinsing
- 35 Drying
- 36 Sodium silicate treatment of metallised beads
- 37 Rinsing
- 38 Amino silane pre-treatment
- 39 Mixing liquid carrier medium
- 40 Add treated metallised (and, if desired, umetallised) beads to carrier medium
- 41 Add pigment

Ink formulations detailed herein, formulated by the methods described, operating as one-pack systems, have long shelf lives, being usable after more than six months, in many cases after more than a year after formulation (based on accelerated ageing measurements at elevated storage temperatures). They show higher initial retroreflectivities at the lower binder/bead volume ratios made possible by the various measures described.

Washfastness and abrasion resistance are acceptable with binder volumes as low as 9% - reducing binder content in the formulation containing polyvinylidene chloride and Trixene actually increases abrasion resistance.

The various novel ingredients and combinations of ingredients each have their contributions to make in connection with the production of one pack inks and while the importance of a binder combined with a coupling agent reacting only at elevated temperature has been particularly noted, it is not intended to suggest that that might be the only novel and inventive subject matter disclosed herein. The pre-treatment of the beads both before and after metallisation also has profound effects even with the binder/coupler systems and is of advantage also in the preparation of inks for printing on substrates which will not withstand elevated temperatures. Here it is necessary to resort to a two-pack system, with the coupling agent mixed into the ink just before printing. A reactive polyisocyanate may be used as a coupling agent in such circumstances. A two-pack arrangement is, of course, more convenient to use than the old three-pack system, and is made possible by bead pre-treatment.

Where unmetallised beads are added - giving the effect, quite obviously, of reducing overall retroreflectivity, but reducing the greyness associated with metallised beads and therefore enhancing the colour brightness of pigmented inks, the unmetallised beads also benefit from the bead pre-treatment.

Unmetallised beads may also be used in similar formulation, and having had similar pre-treatment, without metallised beads but with flake particles having a mirror-like finish. Such a coating composition, said to be suitable for application by brushing, was described in US 3 835 087, Searight *et al*, issued 10 September 1974, and printing ink of this description is commercially available.

According to the present invention, in another aspect, one-pack inks containing unmetallised glass microspheres and flake particles comprise a liquid carrier medium including binder chemicals for attaching the microbeads and flake particles to a substrate to which the ink is to be applied and a coupling agent which couples the

microbeads and cross-links the binder chemicals, characterised in that the coupling agent is unreactive except at elevated temperature at which the ink of the substrate is cured.

Binder and coupler systems as described above are suitable, and the microbeads benefit in the same way from the sodium silicate and amino silane pre-treatment - the stannous chloride pre-treatment is unnecessary.

A preferred flake material is Iriodin 123 - mica flake coated with titanium dioxide, supplied by Merck. The optimum particle size is 5-35 microns, and the flake may be present in an amount about 7.5% by weight.

Mean glass microbead size may be 60 micron - larger beads, e.g. up to 70 micron and larger may be used but may not be suitable for finer screen printing mesh sizes. Good quality, e.g. 1.9 refractive index, beads give better results than lower refractive index beads, and best results are obtained using 60 micron TSTF (twice sieved twice fired) beads.

Coloured reflectivity can be achieved by using interference pigments (Iriodin 200 series), while gold lustre mica pigments (Iriodin 300 series) and metal lustre pigments (Iriodin 500 series) give interesting effects particularly when printed on coloured fabrics.

Table 6 lists ingredients for a range of such inks.

**Table 6**

<b>Ingredient/Ink reference</b>	<b>NMB155</b>	<b>NMB182</b>	<b>NM B185</b>	<b>NMB191</b>
Urea (Humecant)	10	10	10	10
Water	79	134	94	91
Ammonium phosphate buffer	20	20	20	--
Sodium phosphate buffer	--	--	--	10
Emulsifier WN (Dispersant)	--	3	2	3
Emulsifier HVN (Dispersant)	--	--	2	--
Alcoprint PDN (Dispersant)	2	--	--	--
Agitan 218 (Defoamer)	2	2	2	2
Alcoprint PSM (Softener)	30	--	--	30
Alcopriny PT21 (Thickener)	4	4.8	3.3	3
2,3 Propane diol (Humectant)	25	25	25	25
Alcoprint PFL (Cross-linker)	15	--	--	--
Alcoprint PBA (Binder)				
[acrylic]	300	--	--	--
Polidene 33-048 (Binder)				
[polyvinylidene chloride]	--	300	300	--
Witcobond 769 (Binder)				
[polyurethane]	--	--	--	300
Trixene BI-7986 (Coupling agent)	--	--	40	50
Ammonium hydroxide	1	1.4	1.4	--
Silquest VS-142 (Coupling agent) [20% in water]	25	25	25	--
Alcoprint PT21 (Thickener)	3.5	--	--	1
Iridin 123 [Mica coated with titanium dioxide]	75	75	75	75
Beads (60 micron) treated with sod.sil.+ A-1170	400	400	400	400
<b>Total weight (g)</b>	<b>991.5</b>	<b>1000.2</b>	<b>999.7</b>	<b>1000.0</b>
Viscosity (pascals)	23.6			
pH	8.5			

### CLAIMS

1. A one-pack retroreflective ink comprising retroreflective microbeads in a liquid carrier medium including binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied, and a coupling agent which couples the microbeads and cross-links the binder chemicals, characterised in that the coupling agent is unreactive except at elevated temperature at which the printed substrate is cured.
2. An ink according to claim 1, comprising non-retroreflective microbeads.
3. An ink according to claim 1 or claim 2, in which the binder system comprises polyvinylidene chloride copolymer and the coupling agent comprises (3-aminopropyl) silanetriol.
4. An ink according to claim 1 or claim 2, in which the binder system comprises an acrylic copolymer and the coupling agent comprises (3-aminopropyl) silanetriol.
5. An ink according to any one of claims 1 to 4, in which the binder system comprises polyvinylidene chloride copolymer and the coupling agent comprises blocked 1, 6 hexamethylene diisocyanate trimer.
6. An ink according to claim 1 or claim 2, in which the binder system comprises polyurethane and the coupling agent comprises blocked 1, 6 hexamethylene diisocyanate trimer.
7. An ink according to any one of claims 1 to 6, in which the microbeads have an aluminium coating.

8. An ink according to any one of claims 1 to 7, in which the microbeads are pre-treated with a silicate before inclusion in the ink.
9. An ink according to claim 8, in which the silicate is sodium silicate.
10. An ink according to claim 8 or claim 9, in which the microbeads are treated with an amino silane after the silicate pre-treatment and before inclusion in the ink.
11. An ink according to claim 10, in which the microbeads are treated with bis-*[gamma*-(trimethoxysilyl) propyl] amino.
12. An ink according to any one of claims 1 to 11, comprising pigment.
13. An ink according to any one of claims 1 to 12, in which the retroreflective microbeads are pre-treated before metallisation with stannous chloride.
14. An ink according to any one of claims 1 to 13, formulated suitably for screen printing.
15. An ink according to any one of claims 1 to 14, in which the microbeads are 40 micron beads.
16. An ink according to any one of claims 1 to 15, in which the microbeads are of 1.9 refractive index glass.
17. An ink according to any one of claims 1 to 16, comprising a humectant.



18. An ink according to claim 17, in which the humectant comprises urea and/or 2,3 propone diol.
19. An ink according to any one of claims 1 to 18, being water-based.
20. An ink according to any one of claims 1 to 19, comprising a buffer.
21. An ink according to claim 20, in which the buffer comprises an ammonium phosphate buffer.
22. An ink according to claim 20, in which the buffer comprises a sodium phosphate buffer.
23. An ink according to any one of claims 1 to 22, comprising a dispersant.
24. An ink according to any one of claims 1 to 23, comprising a defoamter.
25. An ink according to any one of claims 1 to 24, comprising a thickening agent.
26. An ink according to any one of claims 1 to 25, comprising a cross-linking agent.
27. An ink according to any one of claims 1 to 26, comprising a softening agent.
28. An ink according to any one of claims 1 to 28, of which the binder volume to bead volume ratio is equal to or less than 50%.

29. An ink according to any preceding claim, of which the viscosity is less than or equal to 40 pascals at room temperature.

30. A method for making a one-pack retroreflective ink comprising the steps of:

- making microbeads;
- suspending the microbeads in a liquid carrier medium;
- the liquid carrier medium comprising binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied and a coupling agent which couples the microbeads and cross-links the binder chemicals, the coupling agent being unreactive except at elevated temperature at which the printed substrate is cured.

31. A method according to claim 30, comprising applying an aluminium coating to the microbeads.

32. A method according to claim 31, comprising pre-treating the microbeads with stannous chloride prior to application of the aluminium coating.

33. A method according to claim 32, in which the microbeads are treated with a dilute aqueous solution of stannous chloride.

34. A method according to any one of claims 30 to 33, in which the microbeads are hemispherically metallised in a vacuum metallising process in which they are held

on a film with an adhesive coating for transport through the metallising process the adhesive coating comprising a styrene/butadiene type adhesive.

35. A method according to claim 34, the film comprising a polyester film.

36. A method according to claim 34, or claim 35, in which, following metallisation, the film is passed through an aqueous solution of citric acid.

37. A method according to any one of claims 34 to 36, in which the film is treated ultrasonically to assist in release of the microbeads from the adhesive surface.

38. A method according to any one of claims 36 to 37, in which the metallised microbeads are treated prior to inclusion in the ink with a silicate.

39. A method according to claim 38, in which the microbeads are treated with a dilute aqueous solution of sodium silicate.

40. A method according to any one of claims 30 to 39, in which the microbeads are treated with an amino silane prior to inclusion in the ink.

41. A method according to claim 38 or claim 39, in which the microbeads are treated with an amino silane following the silicate treatment.

42. A method according to claim 41, in which the amino silane comprises bis-[*gamma*-(trimethoxysilyl) propyl] amine.

43. A method according to any one of claims 36 to 42, in which an amino silane is added to the liquid carrier medium as coupling agent.

44. A method according to any one of claims 36 to 43, in which a liquid carrier medium is prepared comprising binder chemicals and coupling agent, and the microbeads are added to the medium.

45. A method according to claim 44, in which a pigment is added to the medium containing the microbeads.

46. A method according to claim 44 or claim 45, in which a humectant is incorporated in the medium.

47. A method according to any one of claims 44 to 46, in which a buffer is added to the medium.

48. A method according to any one of claims 44 to 47, in which a dispersant is added to the medium.

49. A method according to any one of claims 44 to 48, in which a defoamer is added to the medium.

50. A method according to any one of claims 44 to 49, in which a thickener is added to the medium.

51. A method according to claim 50, in which a thickener is added to the medium in two steps, namely before and after the addition of the binder and coupler.

52. A method according to any one of claims 44 to 51, in which a softener is added to the medium.

53. A one-pack or a two-pack retroreflective ink comprising microbeads in a liquid carrier medium including binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied, the microbeads being incorporated in the carrier medium, and a coupling agent which couples the microbeads and cross-links the binder, characterised in that the coupling agent is not activated until the ink is printed.

54. An ink according to claim 53, comprising a separate pack for the coupling agent.

55. An ink according to claim 53 or claim 54, in which the coupling agent comprises a reactive polyisocyanate.

56. An ink according to claim 52, in which the microbeads are all or essentially all unmetallised and the ink comprises reflective flake particles.





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